Biological Uptake of Gold King Released Metals in Aquatic Communities

Initial impacts to organisms during passage of the Gold King Mine (GKM) plume would likely have been acute in nature due to the initial pulse exposure. Exposure of fish to acute levels of metals was assessed by comparing plume metal concentrations to acute water quality criteria. For the most part, acute criteria were not exceeded during the plume. Exceptions were aluminum through much of the Animas and parts of the San Juan River, and several hours of excursions above thresholds for arsenic, cadmium, copper, and zinc in the Animas River from Silverton to Bakers Bridge (RK 64). The acute threshold values, however, have inherent assumptions regarding duration of exposure that were generally not met during passage of the GKM plumes. The very high concentrations that characterized the plume lasted for hours but the full plume duration was less than 48 hours and concentrations dropped significantly from peak highs during that time.

Virtually all aquatic biota are known to bioaccumulate metals from their environment. Although some of these metals (e.g., copper and zinc) are essential for the biota's basic metabolic processes and health, other metals (e.g., arsenic, cadmium, and lead) are well known physiological poisons. Even essential metals, however, can be toxic to organisms in high concentrations. Consequently, as part of its integrated assessment of the potential impacts of the GKM release, we assessed whether whole-body metal concentrations in fish could have increased to adverse levels during the passages of the GKM plume.

There are multiple approaches to estimate the bioaccumulation of metals in aqueous ecosystems. The simplest approaches use bioconcentration or bioaccumulation factors (i.e., BCFs if organisms accumulate the chemical only from water, or BAFs if they accumulate the chemical from both water and food, respectively) to predict chemical concentrations in aquatic biota. These approaches assume that the ratio of an organism's whole-body chemical concentration [$C_o(t)$] to the freely dissolved concentration of that chemical [$C_w(t)$] at any time t is a constant, and that $C_o(t) = C_w(t)\times\mathrm{BAF}$. The accuracy of this approach, however, depends on the organism's rates of growth and of chemical uptake and excretion being significantly faster than the rate of change in the dissolved water concentrations to which they are exposed. If this condition is not satisfied, estimated whole-body concentrations can be very uncertain. Because published BCFs and BAFs for metals are not constants but vary inversely with the prevailing dissolved water concentrations (Chapman et al. 1996, McGeer et al. 2003, DeForest et al. 2007), an alternative kinetic approach was adopted for the GKM bioaccumulation assessment.

To this end, EPA's BASS (Bioaccumulation and Aquatic System Simulator) model (Barber 2008, 2012) was used to predict the expected metal concentrations of Animas River fish under background conditions and immediately before, during, and after the passage of the GKM plume. Unlike the chemical partitioning approaches (i.e., BCFs, BAFs etc.), BASS explicitly models the fish's growth and chemical exchanges between its food, feces, and gill water using a system of differential equations to simulate the growth, population dynamics, and bioaccumulation dynamics of age-structured fish communities.

Application of BASS

The BASS model was developed to predict the population and bioaccumulation dynamics of age-structured fish assemblages exposed to hydrophobic organic pollutants and class 1B and 2B and borderline metals that complex with sulfhydryl groups (e.g., cadmium, copper, lead, mercury, nickel, silver, and zinc). For its application to the GKM release, the partitioning algorithm which BASS uses to describe the internal distribution of metals, was updated with a hyperbolic isotherm that allows the fish's free sulfhydryl groups to saturate during environmental exposures (e.g., dissolved concentrations at Silverton). BASS was then applied at Silverton and Durango to estimate whole-body metal concentrations of fish during an average flow year prior to the GKM release and during the passage of the GKM plumes.

Because brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins accounted for over 97% of total fish caught during the 2010 and 2012 Southern Ute Indian Tribe (SUIT) fish surveys of the Animas River between Purple Cliffs and the New Mexico Stateline (Zimmerman 2013), we assumed that these 6 species would reasonably represented the fish communities at both Silverton and Durango.

BASS's auxiliary parameterization software provides users with complete default data sets of bioenergetic and ecological parameters for 621 species of North American fish; it can also configure a default food web for any combination of these species. This software was used to assign all the bioenergetic, ecological, and morphological parameters required by BASS to simulate whole-body concentrations of cadmium, copper, lead, and zinc at Silverton and Durango under expected background condition and during the GKM plumes.

Daily background dissolved metal concentrations were estimated at Silverton and Durango using the daily concentration model described in Chapter 6, which varies metal concentrations as a function of daily river discharge to produce an annual time series of dissolved metal concentrations that respond to spring snowmelt and other water exchanges. For the GKM plume simulations, hourly dissolved metal concentrations were estimated using EPA's empirical plume characterization model.

Observed metal concentrations in Animas River fishes, which were reported by the Southern Ute Indian Tribe (2015) and by U.S. Bureau of Reclamation (USBR 1996), were used to support model evaluation and comparison.

Annual Simulations of Whole-body Metal Concentrations in Fish

Background whole-body metal concentrations of the fish community were modeled for an average one-year time period prior to the GKM release to establish existing metals concentrations in Animas River fishes. These simulations were then compared to the available fish metal concentrations from the middle to lower Animas reported by the Southern Ute Indian Tribe (2015) and the U.S. Bureau of Reclamation (1996). Although only the most important highlights of these simulations are presented and discussed in the following paragraphs, Appendix E summarizes the full details of these simulations with supporting graphic and tabular results.

Because bioaccumulation dynamics of fish are strongly affected by their ecology, physiology, and body sizes, the 2-3 year old brown trout was selected as a standard fish to simplify certain aspects of the following discussion. For other aspects of this analysis, however, the entire fish community of concern was used (i.e., all age classes of brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins).

Fig. 7-1 displays the background whole-body metal concentrations simulated by BASS for a 2-3 year old trout at Silverton and Durango. Each of these plots show a rapid initial uptake of metals during the first week of October which is a transient feature of these simulations due to assuming zero initial whole-body concentrations for all fish and metal. Although different in their magnitudes, each plot also shows an identifiable response to the April-July snowmelt when total fractions of metals increase but dissolved fractions typically decrease with increased flow. With the exception of copper at Durango (Fig. 7-1b), BASS-simulated whole-body metal concentrations all decease during this period. Whereas the most pronounced decreases were predicted for cadmium, copper, and lead at Silverton, only small decreases were predicted for cadmium, lead, and zinc at Durango.

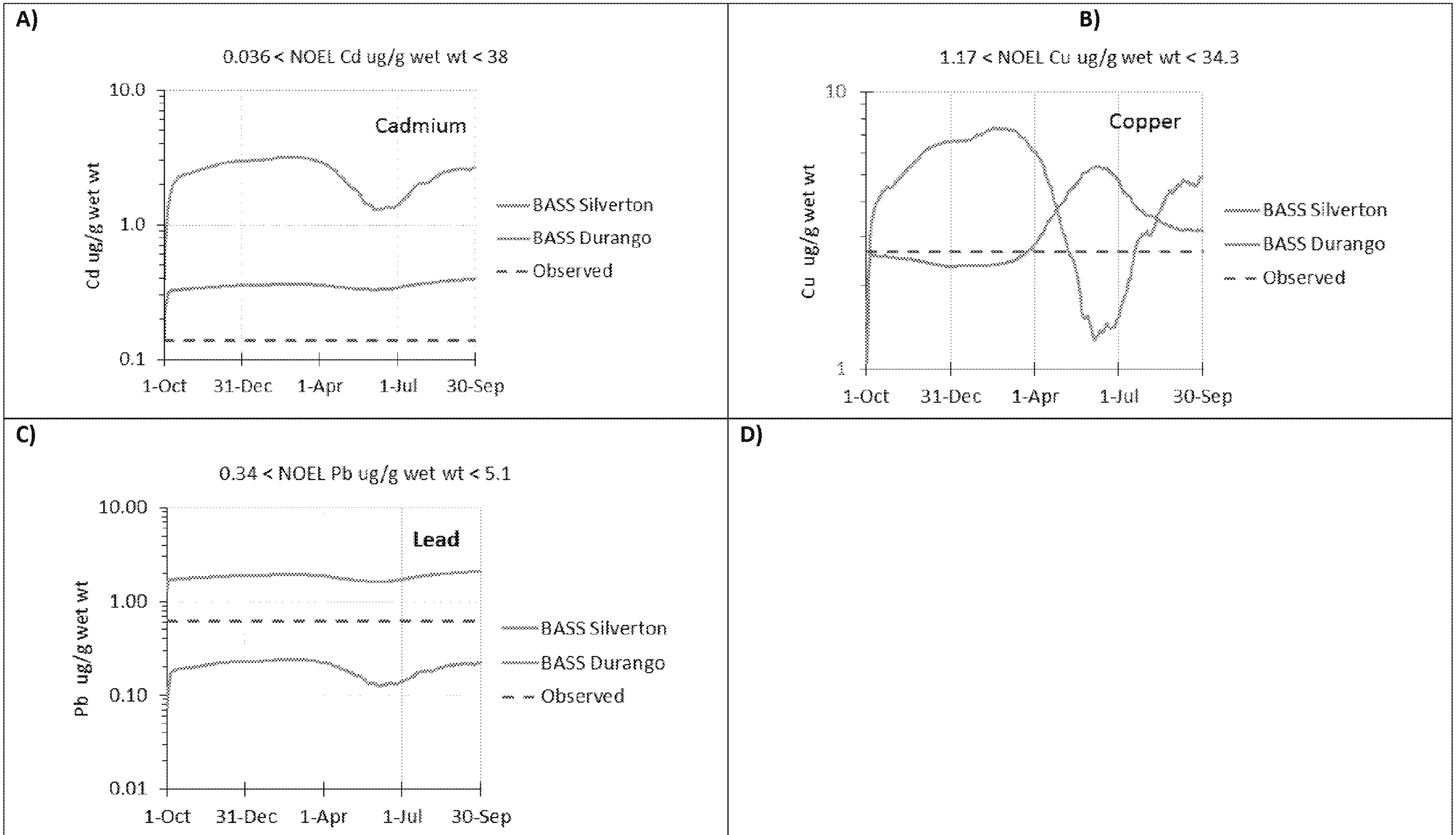

Figure 7-1. Annual dynamics of background whole-body metal concentrations (ug/g wet wt) in 2-3 year old brown trout simulated by BASS for an average flow year at Silverton and Durango compared to the mean field concentration observed in the Animas River (SUIT 2015, USBR 1996). Also shown is the range of whole-body residue-based NOELs (No Observed Effects Levels) for growth, mortality, and reproduction effects in fish compiled by Jarvinen and Ankley (1999) and by CH2MHILL (2015). A.) Cadmium, B.) Copper, C.) Lead D.) Zinc.

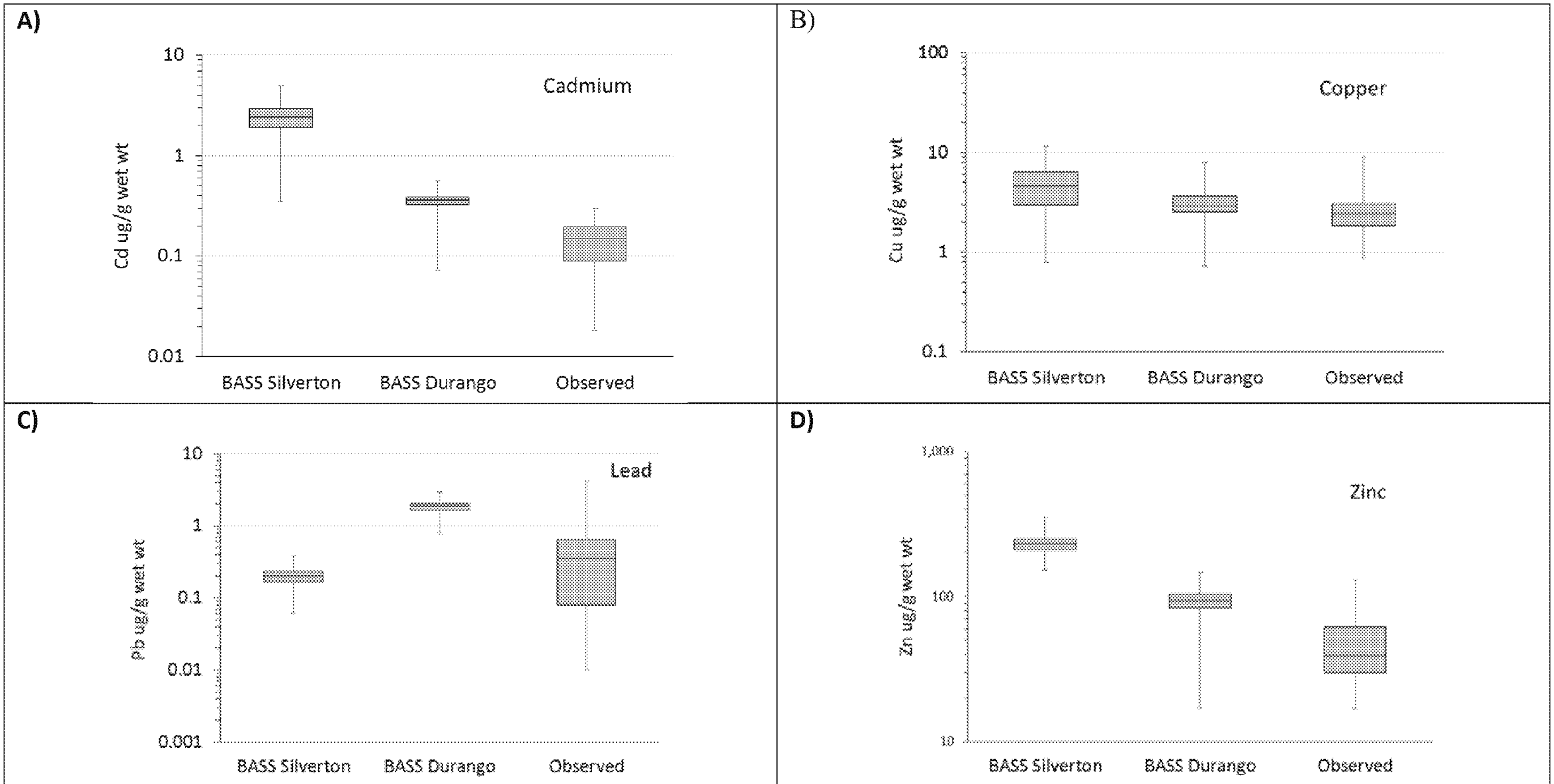

Figure 7-2. Box plots of annual background whole-body metal concentrations (ug/g wet wt) in all age classes of brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins simulated by BASS during an average flow year compared to field concentrations observed in the Animas River (SUIT 2015, USBR 1996). The top and bottom of each box corresponds to the first and third quartiles of the data, respectively; the box's midline is the data's second quartile (i.e., median); and the upper and lower bars or "whiskers" denote the data's maximum and minimum, respectively. A) Cadmium, B) Copper, C) Lead, D) Zinc.

The distributional characteristics of the simulated background whole-body concentrations in all age classes of brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins are displayed in Fig. 7-2 with box plots. The top and bottom of each box corresponds to the first and third quartiles of the data, respectively; the line inside the box is the data's second quartile (i.e., median); and the upper and lower bars or "whiskers" denote the data's maximum and minimum, respectively. Box plots of the observed whole-body concentrations of fish in the middle Animas River provided by the Southern Ute Indian Tribe (SUIT 2015) and the U.S. Bureau of Reclamation (USBR 1996) are also shown in these figures. There was reasonably good agreement between simulated and observed concentrations, especially at Durango where the ambient water concentrations are similar to (but somewhat higher) those on the SUIT reservation.

With the exception of lead, these plots show that whole-body metal concentrations declined from Silverton (RK 16.4) to Durango (RK 94 in this study) and from Durango into SUIT reservation (RK 100 to 132). Whereas copper declines are very modest, the declines in cadmium and zinc concentrations were very pronounced and could be readily attributed to the differences in ambient concentrations of these metals in the upper and middle Animas River. Although lead concentrations in Silverton fish were lower than those at Durango, lead concentrations in Durango fish appear to be distinctly higher than those in fish from the SUIT reservation reaches.

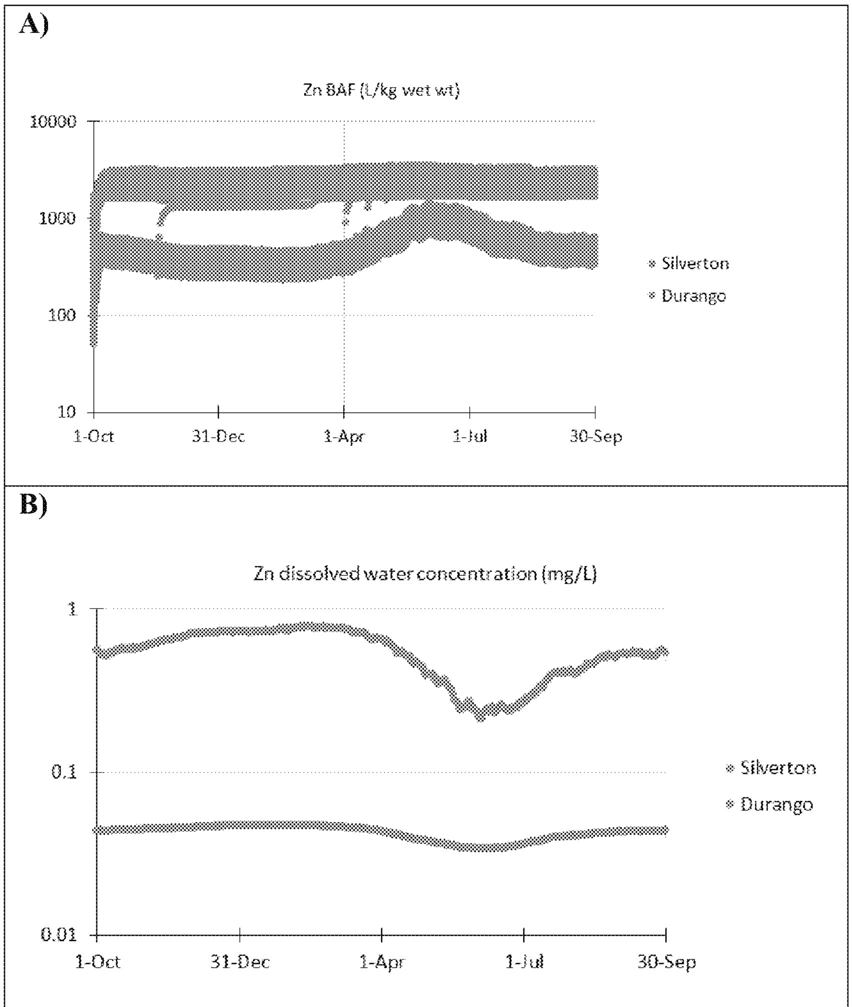

Figure 7-3. Simulated dynamics of zinc BAFs (L/kg wet wt) for all age classes of brown and rainbow trout; bluehead, flannelmouth, and white suckers; and mottled sculpins simulated by BASS during an average flow year. Also shown are dynamics of the empirically estimated dissolved water concentrations (mg/L).

Published metal BAFs are highly variable and generally inversely dependent on the environmental water concentrations used to calculate them (Chapman et al. 1996, McGeer et al. 2003, DeForest et al. 2007). During much of the year when water concentration varies relatively little, BAFs are relatively constant and could be used to estimate metals concentrations in fish with some confidence. Rapidly varying concentrations, however, make constant BAFs problematic. This is most evident with zinc at Silverton during snowmelt; see Fig. 7-3. At this location, fish are near saturation with respect to zinc.

Consequently, as dissolved zinc concentrations decrease during snowmelt calculated fish BAF's must increase resulting in the classic inverse relationship between exposure and body concentrations. It is also important to note that "constant" zinc BAFs from December 31 to April 1 at Silverton and Durango also demonstrate this classic inverse relationship between exposure and body concentrations. In particular, although Durango has much lower dissolved zinc concentrations than does Silverton, its fish have much higher calculated BAFs.

Animas River fishes respond rapidly to metals in their environment. The half -life of metals in these fish vary between 3 and 16 days depending on metal and location (Table 7-1). The half-lives of BASS-simulated whole body concentrations during the average flow year simulations are provided in Table 7-1. Differences between Silverton and Durango partially reflect higher background concentrations at Silverton and significantly lower water temperature which strongly affects bioaccumulation kinetics.

Table 7-1. Summary statistics for the BASS-simulated half-lives of cadmium, copper, lead, and zinc in fish and Silverton and Durango during an average flow year.

Metal	Site	Mean	Median	Standard Deviation	Minimum	Maximum
Cd	Durango	11.6	6.90	7.2	0.21	70.5
Cd	Silverton	16.0	10.4	14.3	0.28	63.8
Cu	Durango	8.21	4.83	8.71	0.15	50.8
Cu	Silverton	11.2	7.26	10.2	0.20	45.5
Pb	Durango	4.91	2.86	5.25	0.09	30.9
Pb	Silverton	6.79	4.32	6.21	0.12	27.9
Zn	Durango	13.6	8.14	13.9	0.25	79.9
Zn	Silverton	3.24	2.61	2.40	0.09	11.1

Metal Bioaccumulation During the GKM Plumes

BASS was used to model the responses of fish communities to the Gold King plume in the Animas River at Silverton and Durango using the empirically modeled plume water concentrations. The plume varied in length from approximately 14 hours at Silverton to 40 hours at Durango, and dissolved metals concentrations ranged over several orders of magnitude at Silverton and at least 1 order of magnitude at Durango. The BASS simulations of whole body concentrations are displayed in Figure 7-4.

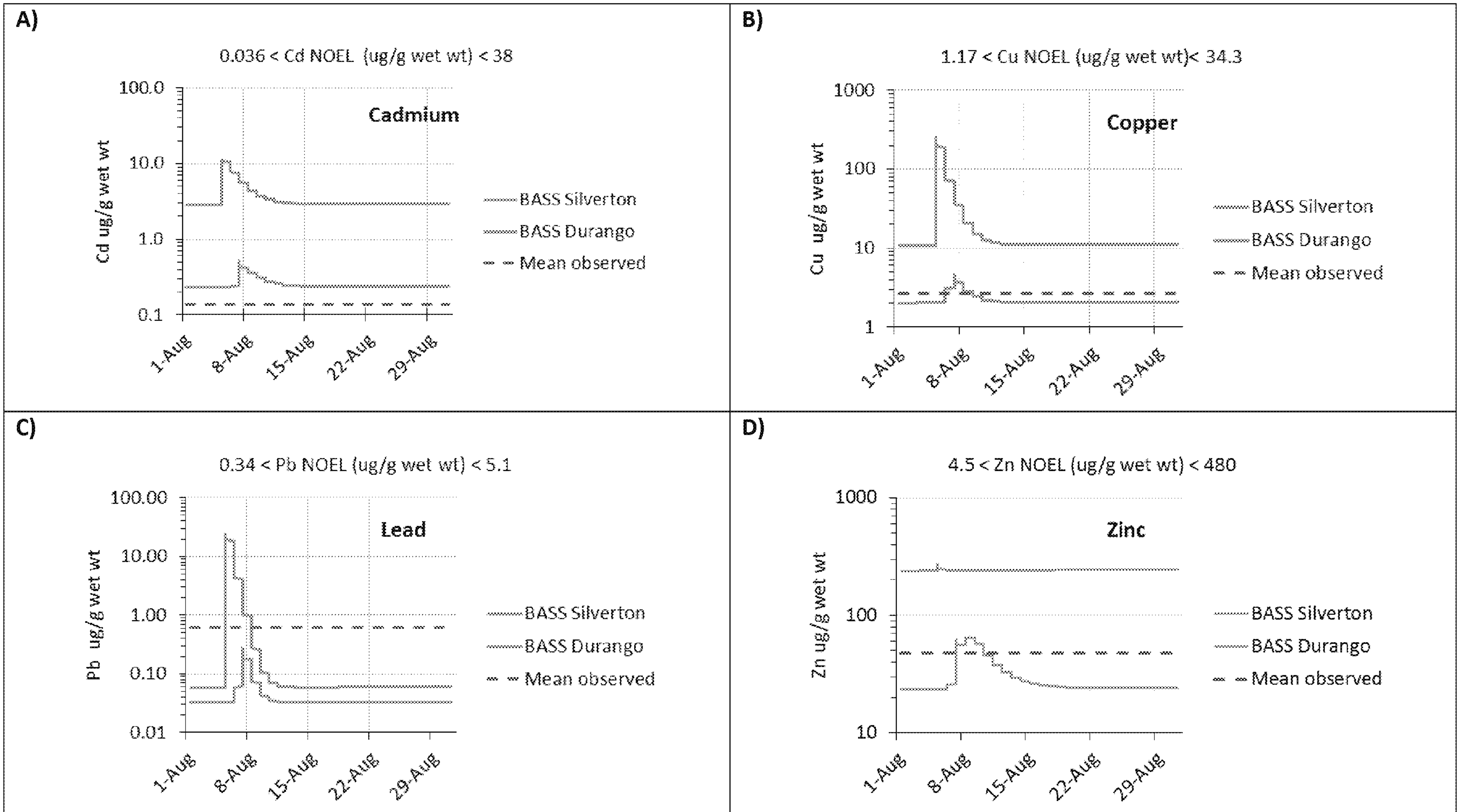

Figure 7-4. GMK plume dynamics of whole-body metal concentrations (ug/g wet wt) in 2-3 year old brown trout at Silverton simulated by BASS compared to mean observed concentrations (SUIT 2015; USBR 1996). A) Cadmium, B) Copper, C) Lead, D) Zinc

BASS predicted that despite the relatively rapid passage of the GKM plumes, the fish likely responded by accumulating metals quickly. The notable exception to this forecast was zinc bioaccumulation at Silverton, where only a very small response to the large concentrations of metals was predicted. Here, fish are already near saturation levels for zinc from chronic exposures. Consequently, they would unlikely to respond significantly to the additional zinc loadings represented by the Gold King plume. Zinc stays within the aqueous phase within the fish and is very mobile so the fish gives it up easily.

Elevated levels were short-lived as the fish also depurated the metals quickly. It generally required about 4 half-lives to completely eliminate the metals accumulated as the GKM plume passed. Most metals were eliminated in about 8 to 12 days after the passage of the plume at Silverton (August 13) and Durango (August 19) respectively.

As predicted for the background BAFs of metals during snowmelt, metal BAFs calculated for fish during the GKM plumes and Silverton and Durango are inversely related to their instantaneous dissolved water concentrations. Table 7-2 summarizes the regression equations that can be used to characterize and to calculate BAFs during the passage of these plumes.

Table 7-2 Summary of the regressions characterizing the relationship between the instantaneously realized $\log_{10}$ BAFs simulated by BASS and their associated dissolved water concentrations (C_w mg/L) during the passage of the GKM plumes at Silverton and Durango using linear model $\log_{10}$ BAF = a + b $\log_{10} C_w$.

Metal	Site	a	b	r^2 adjusted	SE
Cd	Durango	-0.525	-1.02	0.928	0.103
Cd	Silverton	0.719	-1.06	0.923	0.142
Cu	Durango	0.499	-1.01	0.924	0.0709
Cu	Silverton	2.17	-0.976	0.885	0.347
Pb	Durango	-0.852	-0.984	0.773	0.221
Pb	Silverton	0.840	-1.02	0.819	0.579
Zn	Durango	1.61	-1.02	0.890	0.125
Zn	Silverton	2.39	-0.972	0.982	0.0578

Ecological Impacts due to Metal Bioaccumulation

One way to evaluate the potential effects of the GMK plumes of exposed fishes is to compare their accumulated whole-body concentrations to observed whole-body concentration that are known to have caused either no observable ecological effects or quantifiable ecological impacts. The use of such comparisons is based on the simple assumption that chemical concentrations which are internal to an organism are inherently more accurate for assessing onset of toxic responses in organisms than are external environmental concentrations or benchmarks (e.g., LC_{50}).

Table 7-3 summarizes whole-body residue-based NOELs (No Observed Effects Levels) for growth, mortality, and reproduction effects on juvenile and adult fish that EPA complied for this assessment. Table 7-4 summarizes compiled whole-body residue-based OELs (Observed Effects Levels) for growth, mortality, and reproduction effects on juvenile and adult fish.

Background whole-body concentrations of all metals in 2-3 year old brown trout at both Silverton and Durango were completely within the range of NOELs reported in Table 7-3. In terms of OELs, however, background concentrations of cadmium and zinc in these trout were greater than the minimum OELs [i.e., Lowest Observed Effects Levels (LOELs)] reported in Table 7-4 at both locations. Whereas Silverton trout lead concentrations were higher than the lead LOEL, Durango trout lead concentrations were lower than this benchmark. See Figures 7-1 through 7-4.

Table 7-3. Summary statistics for published whole-body residue-based NOELs (No Observed Effects Levels) for growth, mortality, and reproduction effects on juvenile and adult fish. Data were compiled by Jarvinen and Ankley (1999) and by CH2MHILL (2015). These data suggest that while juvenile and adult fish are exposed to high metal concentration at both Silverton and Durango, it is uncertain whether they would be negatively impacted. Potential impacts on egg and larval hatching and survival, however, were not considered in this residue-based assessment.

Statistic	Cd [ug/g_ww]	Cu [ug/g_ww]	Pb [ug/g_ww]	Zn [ug/g_ww]
Mean	4.60	11.5	2.73	120
Median	1.33	8.98	2.54	60
Stan. Deviation	7.50	11.8	1.51	144
Minimum	0.036	1.17	0.34	4.5
Maximum	38	34.3	5.1	480
Sample size	54	6	7	13

Table 7-4. Summary statistics for published whole-body residue-based OELs (Observed Effects Levels) for growth, mortality, and reproduction effects on juvenile and adult fish. Data were compiled by Jarvinen and Ankley (1999) and by CH2MHILL (2015). These data suggest that while juvenile and adult fish are exposed to high metal concentration at both Silverton and Durango, it is uncertain whether they would be negatively impacted. Potential impacts on egg and larval hatching and survival, however, were not considered in this residue-based assessment.

Statistic	Cd [ug/g_ww]	Cu [ug/g_ww]	Pb [ug/g_ww]	Zn [ug/g_ww]
Mean	7.0	21.6	4.4	55.9
Median	4	11.7	4	59.8
Stand. Deviation	17.0	17.7	4.2	11.3
Minimum	0.12	11.1	0.4	40
Maximum	77	42	8.8	68
Sample size	35	3	3	6

During the GKM plume at Durango, whole-body concentrations of all metals in 2-3 year old brown trout were within the range NOELs reported in Table 7-3. During the Silverton plume, however, only cadmium and zinc concentrations in exposed trout were within this range of NOELs. In terms of LOELs, whole-body metal concentrations of Silverton and Durango trout exceeded all assumed LOELs with the exception of copper concentrations at Durango. See Figures 7-1 through 7-4.

Because there is a wide range of NOELs and OELs reported for the metals in Tables 7-3 and 7-4 which overlap significantly, there is no one critical body residue (CBR) or CBR-like threshold for each metal and fish species. Rather, depending on the endpoint of concern (i.e., survival, growth, reproduction, etc.), there is a range of CBRs which are useful in making objective and well defined ecological risk assessments. These CBRs, however, will vary not only by the species of concern but also by that species life history (i.e., age, body weight, trophic position etc.) and exposure history. Although this approach has uncertainties and variability, it can be combined with other information (e.g., water quality thresholds etc.) to make objective assessments and decisions.

Although major ecological impacts on Gold King plume-exposed fish would not expected at either Silverton or Durango based on the preceding NOEL comparisons of BASS-predicted whole-body metal concentrations, it is also clear that these fishes are probably ecologically compromised chronically based on known ranges of OELs based on bioaccumulation modeling. This analysis only analyzed published whole-body NOELs and OELs for the growth, mortality, and reproduction of juvenile and adult fish. Impacts on egg and larval hatching and survival were not considered. Nevertheless, this assessment is consistent with that of Besser and Leib (2007) who concluded that fish populations in the upper Animas at Silverton are impaired by chronic acid mine drainage, especially as related to zinc and copper.

Studies of fish and benthic communities have been conducted in the Animas River following the Gold King plume. The Mountain Studies Institute recently released a report on studies of benthic macroinvertebrates (BMI) communities in the upper Animas River following the Gold King release through the Fall 2015 (MSI 2016). This study found benthic macroinvertebrate populations in the Animas River from Silverton to Durango appear to have largely survived exposure to high metal concentration associated with the Gold King Mine release. Additionally, Colorado Parks and Wildlife data indicate that fish populations in the Animas River were not impacted by the Gold King Mine release (White 2016). All species present before the plume were present after the plume, and there were no differences in BMI community health metrics from 2014 to 2015. They note however, that copper tissue concentrations were higher in 2015 than in 2014 at all sites affected by the Gold King Mine release. This result was consistent with this bioaccumulation analysis.